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(72) Inventors: Hideo DAIMON et al.

(71) Applicant: Hitachi Maxell, Ltd.

SPECIFICATION

1. Title of the Invention: MAGNETIC MEDIUM AND ANODIC OXIDATION MATERIAL

2. Claims

(1) A magnetic recording medium in which a magnetic metal is deposited by plating in anodized Al pores formed by anodizing Al or an Al alloy, the magnetic recording medium having an anodized layer formed of a metal other than Al and Al alloy between a nonmagnetic substrate and an anodized Al or Al alloy layer.

(2) A magnetic recording medium according to Claim 1, wherein the anodized layer formed by a metal other than Al and Al alloy comprises at least one metal selected from the group consisting of Ti, Cr, Zr, Nb, Ta, W, and V.

(3) An anodic oxidation material formed by depositing an Al or an Al alloy layer on a nonmagnetic substrate by physical vapor deposition, the anodic oxidation material having a metal layer formed, by physical vapor deposition, of at

least one metal selected from the group consisting of Ti, Cr, Zr, Nb, Ta, W, and V between the nonmagnetic substrate and the Al or Al alloy layer.

(4) An anodic oxidation material according to Claim 3, wherein the thickness of the Al or Al alloy layer is in the range of 0.1 to 5 μm, and the thickness of the metal underlayer formed of at least one metal selected from the group consisting of Ti, Cr, Zr, Nb, Ta, W, and V is in the range of 0.03 to 0.5 μm.

(5) An anodic oxidation material according to Claim 3 or 4, wherein the nonmagnetic substrate is an organic polymer film.

3. Detailed Description of the Invention

[Technical Field]

The present invention relates to a magnetic recording medium in which a magnetic metal is deposited by plating in pores formed by anodized Al or an Al alloy. More specifically, the present invention relates to an improvement of productivity of the magnetic recording media and to an increase of film adhesion.

[Related Arts]

Magnetic recording media in which a ferromagnetic metal is deposited by plating in anodized Al pores have excellent corrosion resistance and durability, and they have recently been though of for a new material.

[Problems to be Solved by the Invention]

In order to deposit a metal in the pores, alternating-current plating is generally used. This is because an anodized Al layer and an Al layer form, in the interface therebetween, an insulating layer referred to as a barrier layer which makes direct-current plating impossible.

However, alternating current results in a plating efficiency lower than that of direct current, and has a cost disadvantage. Also, when a starting material comprising a nonmagnetic substrate provided with an Al layer thereon by physical vapor deposition is anodized and plated with Fe, the Al layer is liable to peel from the substrate because the adhesion between the Al layer and the substrate is low.

An object of the present invention is to make it possible to deposit a metal in the anodized Al pores by direct-current plating in order to increase productivity, and to increase the adhesion between Al and the nonmagnetic substrate in order to solve the problem of peeling during anodic oxidation and plating.

[Means for Solving the Problems]

The above-described problems are solved by providing an anodic oxidation material disposed at least one metal selected from the group consisting of Ti, Cr, Zr, Nb, Ta, W, and V under an Al or Al alloy layer, and by anodizing the anodic oxidation material from the surface of the Al to the metal underlayer.

[Operation]

When Al is anodized in an aqueous solution of sulfuric acid, oxalic acid, phosphoric acid, or the like, a barrier layer is formed at the bottom of the pores substantially in proportion to the amount of electrolysis current. This barrier layer is a closely packed Al_2O_3 insulating layer, which is non-conductive and amorphous. Therefore, the ferromagnetic metal in the pores can be plated using alternating current, but not using direct current.

For example, if a cross section of a sample anodized in a sulfuric acid solution at an electrolysis current of 15 V is observed by transmission electron microscopy, a formed barrier layer of about 250 Å in thickness will be seen.

However, if an underlayer is formed of a metal, such as Ti, under the Al layer, and anodic oxidation is performed up to the metal underlayer, the barrier layer will not be formed. Since the anodized metal layer formed by anodizing the metal underlayer formed of, for example, Ti is conductive, it can serve as an electrode in a plating process.

Therefore, in a sample which was subjected to anodic oxidation up to the metal underlayer formed of, for example, Ti, a ferromagnetic metal can be deposited by direct-current plating, and thus plating efficiency can be increased.

Also, if the Al layer and the nonmagnetic substrate are

separated by the metal underlayer formed of, for example, Ti, the adhesion between the Al layer and the nonmagnetic substrate increases in comparison with when the Al layer is directly deposited on the nonmagnetic substrate. Hence, peeling does not occur during anodic oxidation and plating.

The thickness of the metal underlayer such as Ti is suitably in the range of 0.03 to 0.5 μm. A thickness of less than 0.03 μm does not allow the anodized layer to grow sufficiently during the anodic oxidation, and consequently, the barrier layer remains. Also, a thickness of more than 0.5 μm does not produce any additional effect and is, accordingly, wasteful.

The thickness of the Al or Al alloy layer disposed on the metal underlayer, such as Ti, is generally in the range of 0.1 to 5 μm. A thickness of less than 0.1 μm does not allow Al crystals to grow sufficiently, and consequently, regularly arranged cells are not formed during the anodic oxidation. A thickness of more than 5 μm excessively increases stiffness, and this is undesirable. In particular, in order to use this material for magnetic tapes, the thickness of the Al or Al alloy layer is preferably 0.5 μm or less, from the viewpoint of flexibility.

The underlayer and the Al or Al alloy layer can be deposited on the surface of the nonmagnetic substrate by physical vapor deposition. The physical vapor deposition

includes vacuum deposition, ion plating, sputtering, ion-beam deposition, and chemical vapor deposition (CVD).

Preferably, before depositing the metal underlayer, the nonmagnetic substrate is subjected to plasma treatment to further increase the adhesion between the underlayer and the nonmagnetic substrate.

Since anodic oxidation of Al or Al alloy is well known to those skilled in the art, it is not particularly described here.

Exemplary nonmagnetic substrates used for the magnetic recording medium of the present invention include Al substrates, organic films such as polyimide and polyethylene terephthalate, glass, ceramics, anodized Al, metal plates such as brass, Si single-crystal plates, and Si single-crystal plates whose surface is thermally oxidized. Organic films are particularly preferable.

The magnetic recording media according to the present invention may be used as magnetic tapes and magnetic disks having a polyester film or a polyimide film serving as the substrate, and magnetic disks and magnetic drums having a disk or drum, serving as the substrate, formed of a synthetic resin film or of Al and glass plates. Also, it can have various structures in which the recording medium comes into contact with a magnetic head and slides.

[Examples]

The present invention will now be further illustrated with reference to Examples.

Example 1

Using a continuous-winding vapor deposition apparatus, a Ti underlayer and an Al layer were deposited in that order on a PET film having a thickness of 20 μm.

The thicknesses of the Ti underlayer and the Al layer were 0.1 μm and 0.3 μm, respectively. The temperature of the substrate was 25°C during the vapor deposition, and the degree of vacuum was 1×10^{-5} Torr during the vapor deposition. The deposition rates of Ti and Al were 350 Å/s and 300 Å/s, respectively.

The structure of the resulting anodic oxidation material is shown in Fig. 1. In the drawing, reference numerals 1, 2, and 3 designate the nonmagnetic substrate formed of the PET film, the Ti layer, and the Al layer, respectively.

The resulting Al/Ti film was subjected to anodic oxidation at a constant current of 1 A/dm^2 in a 1 mol/L sulfuric acid bath. At this moment, the electrolysis time was controlled so that anodic oxidation progresses up to the Al/Ti interface. Next, the sample was placed in a 1% by weight phosphoric acid bath of a temperature of 30°C, and was subjected to anodic oxidation at a small current of 0.04 A/dm^2 for 1 minute and subsequently at a constant voltage of

8 V for 2 minutes.

The cross section of this sample was observed by transmission electron microscopy. As a result, it was shown that an oxidized layer grew beyond the Al/Ti interface to reach 200 Å from the surface of the Ti layer, and that the barrier layer, which had generally been observed, was not present.

Example 2

The anodized layer formed in Example 1 was plated with Fe, acting as a magnetic metal. The plating bath contained 50 g/L of iron (II) ammonium sulfate, 15 g/L of boric acid, and 2 mL/L of glycerin. The pH of the bath was adjusted to 3.0 with diluted sulfuric acid.

The plating was conducted for 10 seconds, using a direct current (-10 V) or an alternating current (sine wave, -10 V, +5 V, 5 to 200 Hz).

Fig. 2 shows saturation magnetization resulting from each plating process. As shown in Fig. 2, when the direct current is applied, a maximum saturation magnetization is exhibited. Hence, it has been shown that this sample can be plated using direct current.

Comparative Example 1

A sample was prepared by depositing only Al at a thickness of 0.3 μm as in Example 1, but the Ti underlayer was not formed, and it was, then, subjected to anodic

oxidation in an identical manner to Example 1. Then, the cross section of the sample was observed by transmission electron microscopy. As a result, a barrier layer of about 250 Å in thickness was seen at the bottom of the pores.

Comparative Example 2

The anodized layer formed in Comparative Example 1 was plated with Fe in an identical manner to Example 2. The results are shown in Fig. 3. The anodized layer was able to be plated at 20 Hz or more of the alternating current, but could not be plated at the direct current.

Example 3

The Fe plating film formed in Example 2 was subjected to a 90-degree bending test (where the sample was repeatedly bent and returned to the original state) to evaluate the adhesion of the film. The results are shown in Table 1.

Comparative Example 3

The sample plated with Fe at 200 Hz in Comparative Example 2 was subjected to the same 90-degree bending test as in Example 3 to evaluate the adhesion. The results are shown in Table 1.

Table 1

(1) Number of times of bending until a peeling results

(2) Example 3

Comparative Example 3

Table 1 shows that the magnetic recording medium of Example 3, which has the Ti underlayer between the nonmagnetic substrate and the Al layer, does not exhibit peeling of the films even though it had been subjected to bending over 15000 times. In contrast, the magnetic recording medium of Comparative Example 3 exhibited peeling of the films when the bending was repeated 32 times.

[Advantages]

As described above, in the structure of the present invention, an underlayer formed of at least one metal selected from the group consisting of Ti, Cr, Zr, Nb, Ta, W, and V is disposed between a nonmagnetic substrate and an Al or Al alloy layer. Anodic oxidation is performed from the surface of the Al or Al alloy layer to the metal underlayer. This conductive metal underlayer makes it possible to deposit a magnetic metal by direct current plating, and thus contributes to increasing the productivity in comparison with when the deposition is performed by conventional alternating current plating.

Also, by providing the metal underlayer, the adhesion to the nonmagnetic substrate can be increased, thus preventing the layers from peeling.

4. Brief Description of The Drawings

Fig. 1 is a sectional view of the principal part of an

anodic oxidation material according to an embodiment of the present invention. Figs. 2 and 3 are graphs showing the relationships between the alternating frequencies applied during Fe plating and the saturation magnetization of the plating film.

1: PET film

2: Ti underlayer

3: Al layer

(1) SATURATION MAGNETIZATION OF PLATING FILM

(2) APPLIED ALTERNATING FREQUENCY

(3) WHEN DC APPLIED

(4) WHEN 5-200 HZ OF AC APPLIED